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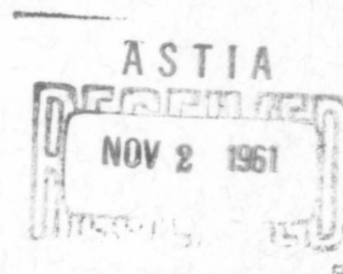
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## A DISCUSSION OF THEORIES OF GRAIN-BOUNDARY DIFFUSION

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JULY 1961

AERONAUTICAL RESEARCH LABORATORY  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE



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# **A DISCUSSION OF THEORIES OF GRAIN-BOUNDARY DIFFUSION**

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## FOREWORD

This report was prepared by C. C. Maneri and F. J. Milford of Battelle Memorial Institute, Columbus, Ohio, on Air Force Contract No. AF 33(616)6265, under Task 70608 "Interactions, Imperfections and Alloy Theory" on Project 7021 "Solid State Research and Properties of Matter". Dr. Maneri is now at the Dept. of Mathematics, University of Chicago, Chicago, Illinois. This work was administered under the direction of the Aeronautical Research Laboratory, Air Force Research Division. Mr. Attwell M. Adair was in charge of the task.

## ABSTRACT

The major theoretical efforts dealing with grain-boundary diffusion have been reconsidered with a view to establishing their mathematical rigor and laying a firm foundation for further work. The details of Whipple's solution to the boundary value problem have been reconstructed and are given in this report. Fisher's approximate solution and its relationship to the exact solution have been considered. A way of evaluating the accuracy of this approximation has been outlined. The work of Borisov et al., has been shown to be equivalent to that of Whipple. Finally, an outline is presented of computational problems directed toward improving our understanding of the relationship of grain-boundary diffusion to the usual model and evaluating various approximations which are frequently used in the study of grain-boundary diffusion.

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## INTRODUCTION

Theories of grain-boundary diffusion invariably begin with the formulation of a boundary-value problem whose solution is expected to describe grain-boundary diffusion. A crucial question is then how well does the solution actually describe the phenomenon. To answer this two things are needed: an accurate experimental study of grain-boundary diffusion and an equally accurate solution of the boundary-value problem. Unfortunately the exact solution of the boundary-value problem is not usually possible in closed form and in the single case where an exact solution is known the form of the solution makes its numerical evaluation extremely difficult. As a result approximate solutions have been developed (in the case being considered the approximate solution antedates the exact solution). This raises another question of a purely mathematical nature, namely how accurate is the approximation.

In this report the boundary-value problem treated by Fisher<sup>(1)</sup> and by Whipple<sup>(2)</sup> has been considered carefully in an attempt to resolve the following questions:

1. Is Whipple's solution, in fact, exact?
2. What are the weaknesses of Fisher's approximate treatment?
3. What is the range of validity of Fisher's approximation?

The first two of these questions have been answered, the second by pointing out that neglecting certain partial derivatives is not admissible under all circumstances. Whipple's solution is shown to be exact by means of a careful reworking of his analysis. The remaining question is partially answered by outlining the calculations needed to justify Fisher's solution.

## WHIPPLE'S SOLUTION

### Statement of the Problem

The idealized situation studied by Whipple<sup>(1)</sup> is that in which the half space,  $y > 0$ , is filled with a material of diffusivity  $D$  except for a thin slab of width  $2a$ . This slab is bounded by the planes  $x = a$  and  $x = -a$ . The diffusivity in this slab is  $D'$  ( $D' \gg D$ ). At time  $t = 0$  the concentration on the surface  $y = 0$  is suddenly raised to unity and maintained at unity. The problem is to find the concentration  $C = C(x, y, t)$  elsewhere.

Let  $C'$  denote the value of  $C$  in the thin slab. Then the diffusion equation says that

$$D' \nabla^2 C' = \frac{\partial C'}{\partial t} \quad (1)$$

in the slab. Outside the slab

$$D \nabla^2 C = \frac{\partial C}{\partial t} \quad (2)$$



It is assumed that for  $t > 0$ ,  $C$  is a continuous function of  $x$  and  $y$ . This means that

$$C' = C \text{ for } x = \pm a. \quad (3)$$

At the boundaries  $x = \pm a$ ,  $\frac{\partial C}{\partial x}$  is discontinuous and satisfies the equation

$$D' \frac{\partial C'}{\partial x} = D \frac{\partial C}{\partial x}. \quad (4)$$

The derivatives involved in Eq. (4) are one sided derivatives and the prime (or lack of one) indicates the direction in which they are taken.

On the surface  $y = 0$ ,

$$C(x, 0, t) = 1 \text{ when } t \geq 0. \quad (5)$$

When  $t = 0$ ,

$$C(x, y, 0) = 0 \text{ if } y > 0. \quad (6)$$

#### Approximate Boundary Condition at $x = a$

An approximate boundary condition on the surface  $x = a$  will now be derived.

Because of the symmetry of the situation  $C'$  is an even function of  $x$ . Hence it can be written as a power series in  $x$  with the odd powers of  $x$  missing. The coefficients are functions of  $y$  and  $t$ .

$$C'(x, y, t) = C'_0(y, t) + \frac{x^2}{2} C'_2(y, t) + \dots \quad (7)$$

When the derivatives

$$\begin{aligned} \frac{\partial C'}{\partial t} &= \frac{\partial C'_0}{\partial t} + \dots, \\ \frac{\partial^2 C'}{\partial y^2} &= \frac{\partial^2 C'_0}{\partial y^2} + \dots, \text{ and} \\ \frac{\partial^2 C'}{\partial x^2} &= C'_2 + \dots; \end{aligned}$$

are substituted in Eq. (1) and terms involving second or higher powers of  $x$  are dropped, one obtains

$$D' \left( \frac{\partial^2 C'_0}{\partial y^2} + C'_2 \right) = \frac{\partial C'_0}{\partial t} \quad (8)$$

for points in the slab (in the applications  $a$  is a very small number).

Again dropping powers of  $x$  which are second or higher there results

$$C = C_0' \text{ and}$$

$$D \frac{\partial C}{\partial x} = D' a C_2' \text{ at } x = a, \quad (9)$$

because of Eq. (3) and Eq. (4) and the fact that

$$\frac{\partial C'}{\partial x} = x C_2' + \dots$$

Now since  $C = C_0'$  at  $x = a$ , and the partial derivatives with respect to  $y$  and  $t$  on the surface  $x = a$  depend only on the common value of  $C$  and  $C_0'$  on this surface,

$$\frac{\partial C}{\partial t} = \frac{\partial C_0'}{\partial t} \text{ and} \quad (10)$$

$$\frac{\partial^2 C}{\partial y^2} = \frac{\partial^2 C_0'}{\partial y^2} \text{ at } x = a.$$

Substituting all of these quantities in Eq. (8) gives

$$D' \frac{\partial^2 C}{\partial y^2} + \frac{D}{a} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \text{ for } x = a. \quad (11)$$

The differential Eq. (2) can be used to write this last equation in a more usable form. Putting  $x = a$  in

$$D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} = \frac{\partial C}{\partial t},$$

which holds for all points outside the slab, and combining this with Eq. (11) gives

$$D' \frac{\partial^2 C}{\partial x^2} - \frac{D}{a} \frac{\partial C}{\partial x} = \left( \frac{D'}{D} - 1 \right) \frac{\partial C}{\partial t} \text{ for } x = a. \quad (12)$$

This is the form in which the approximate boundary condition will be used.

#### The Fourier-Laplace Transform

In order to solve the diffusion equation the function  $C(x,y,t)$  is transformed by both a Fourier and a Laplace transform. The function defined is

$$\Psi(x,\mu,\lambda) = \int_0^\infty \exp(-\lambda t) dt \int_0^\infty \sin(\mu y) C(x,y,t) dy. \quad (13)$$

For purposes of discussion the intermediate function

$$\theta(x, \mu, t) = \int_0^{\infty} \sin(\mu y) C(x, y, t) dy \quad (14)$$

is defined.

The convergence of  $\theta(x, \mu, t)$  will first be determined.

The function  $C(x, y, t)$  is bounded by the value it would have if  $D = D'$ , that is if the material outside the slab had the same diffusivity as the material inside. The solution to this problem is well known.<sup>(5)</sup> It is

$$C = \operatorname{erfc} \left[ \frac{y}{2\sqrt{D't}} \right].$$

Therefore since

$$0 \leq C(x, y, t) \leq \operatorname{erfc} \left[ \frac{y}{2\sqrt{D't}} \right] \quad (15)$$

it can be seen that

$$\int_0^{\infty} C(x, y, t) dy \text{ exists,}$$

and hence

$$\int_0^{\infty} \sin(\mu y) C(x, y, t) dy \text{ exists.}$$

This also gives a bound on  $\theta(x, \mu, t)$ :

$$|\theta(x, \mu, t)| \leq \int_0^{\infty} \operatorname{erfc} \left[ \frac{y}{2\sqrt{D't}} \right] dy = 2\sqrt{\frac{D't}{\pi}}.$$

The second integral,

$$\int_0^{\infty} \theta(x, \mu, t) \exp(-\lambda t) dt,$$

will now be discussed. First it is observed that  $\lambda$  is a complex number with positive real part. This will insure convergence since

$$|\theta(x, \mu, t) \exp(-\lambda t)| \leq 2\sqrt{\frac{D't}{\pi}} \exp(-at)$$

where  $a$  is the real part of  $\lambda$ , and

$$\lim_{t \rightarrow \infty} \left[ 2\sqrt{\frac{D}{\pi}} \exp(-at) \right] \exp\left(\frac{at}{2}\right) = 0.$$

This also shows that  $\Psi(x, \mu, \lambda)$  has a bound which is independent of  $x$  and  $\mu$  (but not  $\lambda$ ).

When the function  $\Psi(x, \mu, \lambda)$  is obtained, it will be seen to possess the correct properties so that the inversion formula

$$\theta(x, \mu, t) = \frac{1}{2\pi i} \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \exp(\lambda t) \Psi(x, \mu, \lambda) d\lambda$$

holds for  $\gamma > 0$ . From the properties on  $C(x, y, t)$  it will be shown that

$$C(x, y, t) = \frac{2}{\pi} \int_0^{\infty} \theta(x, \mu, t) \sin(\mu y) d\mu.$$

#### Transformation of the Differential Equation

When  $C(x, y, t)$  is transformed by the Fourier-Laplace transform, the derivatives  $\partial C / \partial x$  and  $\partial^2 C / \partial x^2$  are transformed into  $\partial \Psi / \partial x$  and  $\partial^2 \Psi / \partial x^2$ , respectively.

The derivative  $\partial^2 C / \partial y^2$  will now be transformed. First it must be observed that

$$\lim_{y \rightarrow \infty} C(x, y, t) = 0, \text{ and}$$

$$\lim_{y \rightarrow \infty} \frac{\partial C}{\partial y} = 0.$$

Then the integration

$$\int_0^{\infty} \sin(\mu y) \left( \frac{\partial^2 C}{\partial y^2} \right) dy \text{ can be performed to give}$$

$$\begin{aligned}
\int_0^{\infty} \sin(\mu y) \left( \frac{\partial^2 C}{\partial y^2} \right) dy &= \sin(\mu y) \left( \frac{\partial C}{\partial y} \right) \Big|_{y=0}^{y=\infty} - \mu \int_0^{\infty} \cos(\mu y) \left( \frac{\partial C}{\partial y} \right) dy \\
&= -\mu \cos(\mu y) C(x, y, t) \Big|_{y=0}^{y=\infty} - \mu^2 \int_0^{\infty} \sin(\mu y) C(x, y, t) dy \\
&= \mu C(x, 0, t) - \mu^2 \int_0^{\infty} C(x, y, t) \sin(\mu y) dy.
\end{aligned}$$

Observing that  $C(x, 0, t) = 1$ , multiplying this last expression by  $\exp(-\lambda t)$ , and integrating gives

$$\begin{aligned}
&\int_0^{\infty} \exp(-\lambda t) dt \int_0^{\infty} \sin(\mu y) \left( \frac{\partial^2 C}{\partial y^2} \right) dy \\
&= \mu \int_0^{\infty} \exp(-\lambda t) dt - \mu^2 \int_0^{\infty} \exp(-\lambda t) dt \int_0^{\infty} C(x, y, t) \sin(\mu y) dy \\
&= \frac{\mu}{\lambda} - \mu^2 \psi(x, \mu, \lambda).
\end{aligned}$$

Thus  $\frac{\partial^2 C}{\partial y^2}$  is transformed into

$$\frac{\mu}{\lambda} - \mu^2 \psi(x, \mu, \lambda).$$

To transform  $\frac{\partial C}{\partial t}$  the integral  $\int_0^{\infty} \exp(-\lambda t) \left( \frac{\partial C}{\partial t} \right) dt$  is evaluated. Because  $C(x, y, 0) = 0$ ,

$$\begin{aligned}
\int_0^{\infty} \exp(-\lambda t) \left( \frac{\partial C}{\partial t} \right) dt &= \exp(-\lambda t) C(x, y, t) \Big|_{t=0}^{t=\infty} + \lambda \int_0^{\infty} \exp(-\lambda t) C(x, y, t) dt \\
&= \lambda \int_0^{\infty} \exp(-\lambda t) C(x, y, t) dt.
\end{aligned}$$

Multiplying by  $\sin(\mu y)$  and integrating gives

$$\int_0^{\infty} \sin(\mu y) dy \int_0^{\infty} \exp(-\lambda t) \left( \frac{\partial C}{\partial t} \right) dt = \lambda \int_0^{\infty} \sin(\mu y) dy \int_0^{\infty} \exp(-\lambda t) C(x, y, t) dt.$$

Thus  $\frac{\partial C}{\partial t}$  is transformed into

$$\lambda \psi(x, \mu, \lambda).$$

From these results it follows that the differential Eq. (2) is transformed into the equation

$$D \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\mu}{\lambda} - \mu^2 \psi \right) = \lambda \psi.$$

Rewriting this gives

$$\frac{\partial^2 \psi}{\partial x^2} - \left( \mu^2 + \frac{\lambda}{D} \right) \psi = - \frac{\mu}{\lambda}. \quad (16)$$

The boundary condition Eq. (12) transforms into

$$D' \frac{\partial^2 \psi}{\partial x^2} - \frac{D}{a} \frac{\partial \psi}{\partial x} = \left( \frac{D'}{D} - 1 \right) \lambda \psi \text{ for } x = a. \quad (17)$$

#### Solution of the Transformed Equation

The function  $\psi(x, \mu, \lambda)$  is to be regarded as a complex function of the real variable  $x$  for fixed  $\mu$  and  $\lambda$ . Then Eq. (16) is essentially an ordinary differential equation in  $x$  with complex coefficients.

The solution of Eq. (16) is

$$\psi(x, \mu, \lambda) = A \exp \left( x \sqrt{\mu^2 + \frac{\lambda}{D}} \right) + B \exp \left( - x \sqrt{\mu^2 + \frac{\lambda}{D}} \right) + E, \quad (18)$$

where  $A$ ,  $B$ , and  $E$  are functions of  $\lambda$  and  $\mu$  and the radical indicates that the square root with positive real part be taken. Since  $\psi$  is a bounded function of  $x$ , we can reject the term

$$A \exp \left( x \sqrt{\mu^2 + \frac{\lambda}{D}} \right).$$

This leaves  $B$  and  $E$  yet to be determined. Because the term

$$B \exp \left( - x \sqrt{\mu^2 + \frac{\lambda}{D}} \right)$$

is a solution of the homogeneous equation

$$\frac{\partial^2 \psi}{\partial x^2} - \left( \mu^2 + \frac{\lambda}{D} \right) \psi = 0,$$

it can be concluded that

$$- \left( \mu^2 + \frac{\lambda}{D} \right) E = - \frac{\mu}{\lambda}$$

and therefore

$$E = \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)} \quad (19)$$

The function B must now be adjusted so that  $\psi$  satisfies the boundary condition Eq. (17) for  $x = a$ . Substituting  $\psi$ ,

$$\frac{\partial \psi}{\partial x} = -B \left( \sqrt{\mu^2 + \frac{\lambda}{D}} \right) \exp \left( -x \sqrt{\mu^2 + \frac{\lambda}{D}} \right),$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = B \left( \mu^2 + \frac{\lambda}{D} \right) \exp \left( -x \sqrt{\mu^2 + \frac{\lambda}{D}} \right)$$

into Eq. (17) when  $x = a$  gives

$$B \left[ D' \left( \mu^2 + \frac{\lambda}{D} \right) + \frac{D}{a} \sqrt{\mu^2 + \frac{\lambda}{D}} - \left( \frac{D'}{D} - 1 \right) \lambda \right] \exp \left( -a \sqrt{\mu^2 + \frac{\lambda}{D}} \right) = \left( \frac{D'}{D} - 1 \right) \frac{\lambda \mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)}.$$

Solving for B one obtains

$$B = \frac{\left[ \left( \frac{D'}{D} - 1 \right) \mu \right] \exp \left[ a \sqrt{\mu^2 + \frac{\lambda}{D}} \right]}{\left( \mu^2 + \frac{\lambda}{D} \right) \left[ D' \mu^2 + \frac{D}{a} \sqrt{\mu^2 + \frac{\lambda}{D}} + \lambda \right]}.$$

Therefore  $\psi(x, \mu, \lambda)$  is determined uniquely to be  $\psi_1 + \psi_2$  where

$$\psi_1 = \frac{\mu}{\lambda \left( \mu^2 + \frac{\lambda}{D} \right)}$$

and

$$\psi_2 = \frac{\left( \frac{D'}{D} - 1 \right) \mu \exp \left[ - (x-a) \sqrt{\mu^2 + \frac{\lambda}{D}} \right]}{\left( \mu^2 + \frac{\lambda}{D} \right) \left[ D' \mu^2 + \frac{D}{a} \sqrt{\mu^2 + \frac{\lambda}{D}} + \lambda \right]}. \quad (20)$$

Inversion of  $\psi_1$

$C_1$  will be used to denote the inverse of  $\psi_1$ . The formula for  $C_1$  is

$$C_1 = \frac{1}{\pi^2 i} \int_0^\infty \mu \sin(\mu y) d\mu \left[ \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \frac{\exp(\lambda t)}{\left( \mu^2 + \frac{\lambda}{D} \right)} \frac{d\lambda}{\lambda} \right]$$

where  $\gamma > 0$ . The value of the quantity in the brackets is easily seen to be independent of  $\gamma$  as long as  $\gamma > 0$ . This will be discussed later.

When the substitutions;

$$y = \eta \sqrt{Dt}, \quad \mu = \frac{\mu'}{\sqrt{Dt}} \text{ and } \lambda = \frac{\lambda'}{t};$$

are made,  $C_1$  reduces to

$$C_1 = \frac{1}{\pi^2 i} \int_0^\infty \mu' \sin(\mu' \eta) d\mu' \left[ \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \frac{\exp \lambda'}{(\mu'^2 + \lambda')} \frac{d\lambda'}{\lambda'} \right].$$

Since the value of  $C_1$  was independent of  $\gamma$  before the substitution the last form is also independent of the choice of  $\gamma$  as long as  $\gamma > 0$ . The primes can be dropped and  $C_1$  can be written

$$C_1 = \frac{1}{\pi^2 i} \int_0^\infty \mu \sin(\mu \eta) d\mu \left[ \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \frac{\exp \lambda}{(\mu^2 + \lambda)} \frac{d\lambda}{\lambda} \right].$$

For the purposes of evaluating the contour integral,  $\lambda$  will be written as  $x + iy$ . (There should be no confusion of this  $x$  and  $y$  with the original  $x$  and  $y$  of the problem.)

The integrand,

$$\frac{\exp \lambda}{(\mu^2 + \lambda) \lambda},$$

is analytic for all values of  $\lambda$  except for  $\lambda = 0$  and  $\lambda = -\mu^2$  where it has simple poles. Therefore the integral of this function about a closed contour which encloses both poles has the value

$$\bullet 2\pi i \left( \frac{1}{\mu^2} - \frac{\exp(-\mu^2)}{\mu^2} \right),$$

since the residue at  $\lambda = 0$  is  $\frac{1}{\mu^2}$  and the residue at  $\lambda = -\mu^2$  is  $-\frac{\exp(-\mu^2)}{\mu^2}$ .

Let the closed contour to be used consist of the line  $x = \gamma$  between the points  $\gamma - iR$  and the point  $\gamma + iR$  and the part of the circle,  $\lambda = R' e^{i\theta}$ , which is to the left of the line  $x = \gamma$ , where  $R' = \sqrt{R^2 + \gamma^2}$ . Call this contour, as shown in Figure 1,  $\Gamma$ . Note that as  $R \rightarrow \infty$  so does  $R'$ . Suppose  $R' > \mu^2$ . Then

$$\int_{\Gamma} \frac{\exp \lambda}{(\mu^2 + \lambda) \lambda} d\lambda = 2\pi i \left[ \frac{1 - \exp(-\mu^2)}{\mu^2} \right]$$



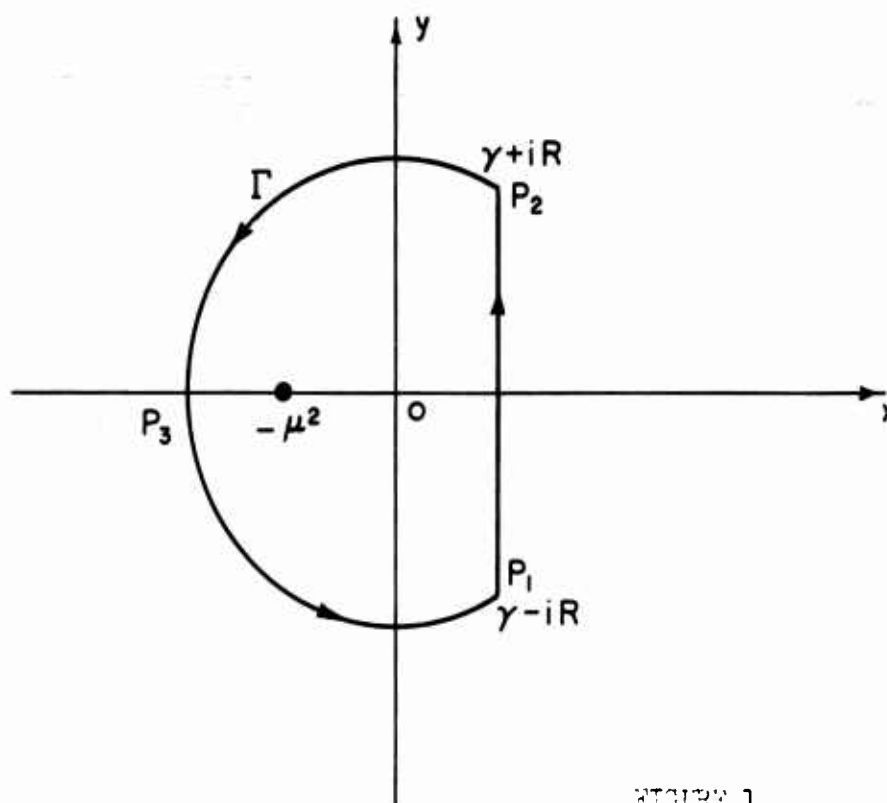


FIGURE 1.

Now as  $R \rightarrow \infty$  it will be seen that the contribution to this integral from the circular part goes to zero. The integrand along this part of  $\Gamma$  is

$$\frac{\exp(R' e^{i\theta})}{(\mu^2 + R' e^{i\theta}) R' e^{i\theta}}.$$

Since the real part of  $\lambda$  on this curve is never greater than  $\gamma$ ,

$$|\exp(R' e^{i\theta})| \leq \exp \gamma$$

on it. The point  $R' e^{i\theta}$  is never closer to the point  $-\mu^2$  than  $R' - \mu^2$ . Thus

$$|\mu^2 + R' e^{i\theta}| \geq R' - \mu^2,$$

and

$$\left| \frac{\exp(R' e^{i\theta})}{(\mu^2 + R' e^{i\theta}) R' e^{i\theta}} \right| \leq \frac{\exp \gamma}{(R' - \mu^2) R'} \text{ on } \Gamma.$$

The length of the curve  $P_2 P_3 P_1$  is less than  $2\pi R'$ ; therefore

$$\left| \int_{P_2 P_3 P_1} \frac{\exp \lambda}{(\mu^2 + \lambda)\lambda} d\lambda \right| < \frac{2\pi \exp \gamma}{(R' - \mu^2)}$$

This integral can be seen to approach zero as  $R \rightarrow \infty$ . Hence

$$\lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \frac{\exp \lambda}{(\mu^2 + \lambda)\lambda} d\lambda = 2\pi i \left[ \frac{1 - \exp(-\mu^2)}{\mu^2} \right].$$

This permits  $C_1$  to be written:

$$\begin{aligned} C_1 &= \frac{2}{\pi} \int_0^\infty \sin(\mu\eta) \left[ 1 - \exp(-\mu^2) \right] \frac{d\mu}{\mu} = \frac{2}{\pi} \\ &\int_0^\infty \frac{\sin(\mu\eta)}{\mu} d\mu - \frac{2}{\pi} \int_0^\eta d\eta' \int_0^\infty \cos(\mu\eta') \exp(-\mu^2) d\mu \\ &= 1 - \frac{1}{\sqrt{\pi}} \int_0^\eta \exp\left(-\frac{\eta'^2}{4}\right) d\eta' = 1 - \operatorname{erf} \frac{\eta}{2} = \operatorname{erfc} \frac{\eta}{2}. \end{aligned}$$

These last integrals may be evaluated from a standard table of integrals, for example, formulas 406 and 432 from the table of integrals of the Handbook of Chemistry and Physics<sup>(8)</sup>.

### Inversion of $\psi_2$

Let  $C_2$  denote the inverse of  $\psi_2$ . Then

$$C_2 = \frac{1}{\pi^2 i} \int_0^\infty \sin(\mu y) d\mu \left[ \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \exp(\lambda t) \psi_2 d\lambda \right],$$

where  $\gamma > 0$ . It will be seen later that  $C_2$  is independent of the choice of  $\gamma$  as long as  $\gamma > 0$ .

The following substitutions will now be made:

$$\xi = \frac{x-a}{\sqrt{Dt}}, \quad \eta = \frac{y}{\sqrt{Dt}}, \quad \alpha = \frac{a}{\sqrt{Dt}}, \quad \Delta = \frac{D'}{D}, \quad \beta = \frac{\Delta - 1}{\sqrt{Dt}} = (\Delta - 1)\alpha, \quad \mu = \frac{\mu'}{\sqrt{Dt}} \text{ and } \lambda = \frac{\lambda'}{t}.$$

$\psi_2$  is reduced by these to

$$\frac{t\sqrt{Dt}(\Delta-1)\mu' \exp\left[-\xi\sqrt{\mu'^2 + \lambda'}\right]}{(\mu'^2 + \lambda')(\Delta\mu'^2 + \frac{1}{a}\sqrt{\mu'^2 + \lambda' + \lambda'})}.$$

When this is put into the expression for  $C_2$  and the substitution completed one obtains

$$C_2 = \frac{(\Delta-1)}{\pi^2 i} \int_0^\infty \mu \sin(\mu\eta) d\mu \left[ \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \frac{\exp(\lambda - \xi\sqrt{\mu^2 + \lambda}) d\lambda}{(\mu^2 + \lambda)(\Delta\mu^2 + \frac{1}{a}\sqrt{\mu^2 + \lambda + \lambda})} \right]$$

after dropping the primes. Note that  $\gamma > 0$  and this expression for  $C_2$  inherits the property of being independent of  $\gamma$ .

It is desirable, however, to take the contour integral along the line  $x = -\mu^2$ . (Again  $\lambda$  is written  $x + iy$  for the contour integration.) The point  $\lambda = -\mu^2$  is a branch point of the integral and must therefore be avoided. The contour which will be used is shown in Figure 2 and is denoted by  $\Gamma(R)$ .

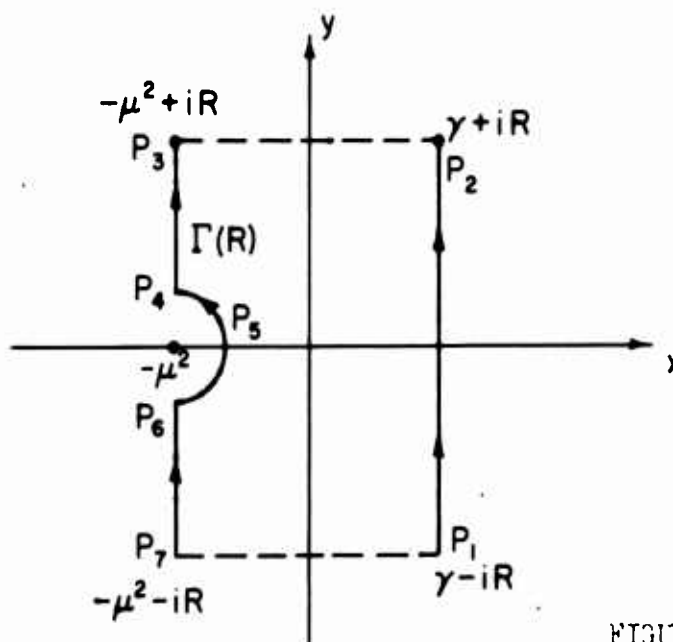


FIGURE 2.

The curved part of  $\Gamma(R)$  is a semi-circle of unit radius with center at the point  $-\mu^2$ , while the rest of  $\Gamma(R)$  consists of the line  $x = -\mu^2$  between the points  $-\mu^2 - iR$  and  $-\mu^2 + iR$ .

The function  $\sqrt{\mu^2 + \lambda}$  is analytic for all values of  $\lambda$  where  $\lambda$  is not real and all real values of  $\lambda$  greater than  $-\mu^2$ . The only zero of  $(\mu^2 + \lambda)$  is at  $\lambda = -\mu^2$ . The function  $\Delta\mu^2 + \frac{1}{\alpha}\sqrt{\mu^2 + \lambda} + \lambda$  is analytic at all points where  $\sqrt{\mu^2 + \lambda}$  is. It cannot be zero if  $\lambda$  has an imaginary component because  $\alpha > 0$  and  $\text{Im}(\sqrt{\mu^2 + \lambda})$  has the same sign as  $\text{Im}(\lambda)$ . It cannot be zero for real  $\lambda$  greater than  $-\mu^2$  because  $\Delta > 1$  and  $\sqrt{\mu^2 + \lambda}$  is a positive real number in this case.

Therefore the function

$$\frac{\exp(\lambda - \xi\sqrt{\mu^2 + \lambda})}{(\mu^2 + \lambda)(\Delta\mu^2 + \frac{1}{\alpha}\sqrt{\mu^2 + \lambda} + \lambda)} = f(\lambda)$$

is analytic at all points on  $\Gamma(R)$  and all points to the right of  $\Gamma(R)$ . From this it follows that

$$\int_{\Gamma(R)} f(\lambda) d\lambda - \int_{\gamma - iR}^{\gamma + iR} f(\lambda) d\lambda = \int_{P_2 P_3} f(\lambda) d\lambda + \int_{P_7 P_1} f(\lambda) d\lambda.$$

Along the segment  $P_2 P_3$ ,  $\lambda = x + iR$  and

$$|\mu^2 + \lambda| \geq R,$$

$$|\Delta\mu^2 + \frac{1}{\alpha}\sqrt{\mu^2 + \lambda} + \lambda| \geq R$$

(because  $\text{Im}(\sqrt{\mu^2 + \lambda})$  has the same sign as  $\text{Im}(\lambda)$ ), and

$$|\exp \lambda - \xi\sqrt{\mu^2 + \lambda}| \leq \exp \gamma$$

(because  $\text{Re}(\sqrt{\mu^2 + \lambda}) \geq 0$ ). This gives that

$$\left| \int_{P_2 P_3} f(\lambda) d\lambda \right| \leq \left[ \frac{\exp \gamma}{R^2} \right] (\gamma + \mu^2)$$

and this goes to zero as  $R \rightarrow \infty$ . A similar argument holds for  $P_7 P_1$ . These

statements show that

$$\lim_{R \rightarrow \infty} \int_{\Gamma(R)} f(\lambda) d\lambda = \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} f(\lambda) d\lambda .$$

The transformation  $v = \sqrt{\mu^2 + \lambda}$  will now be performed on the integral along  $\Gamma(R)$ , where again the radical indicates the square root with positive real part. This transformation takes  $\Gamma(R)$  into the contour  $\Gamma'(R)$  shown in Figure 3.

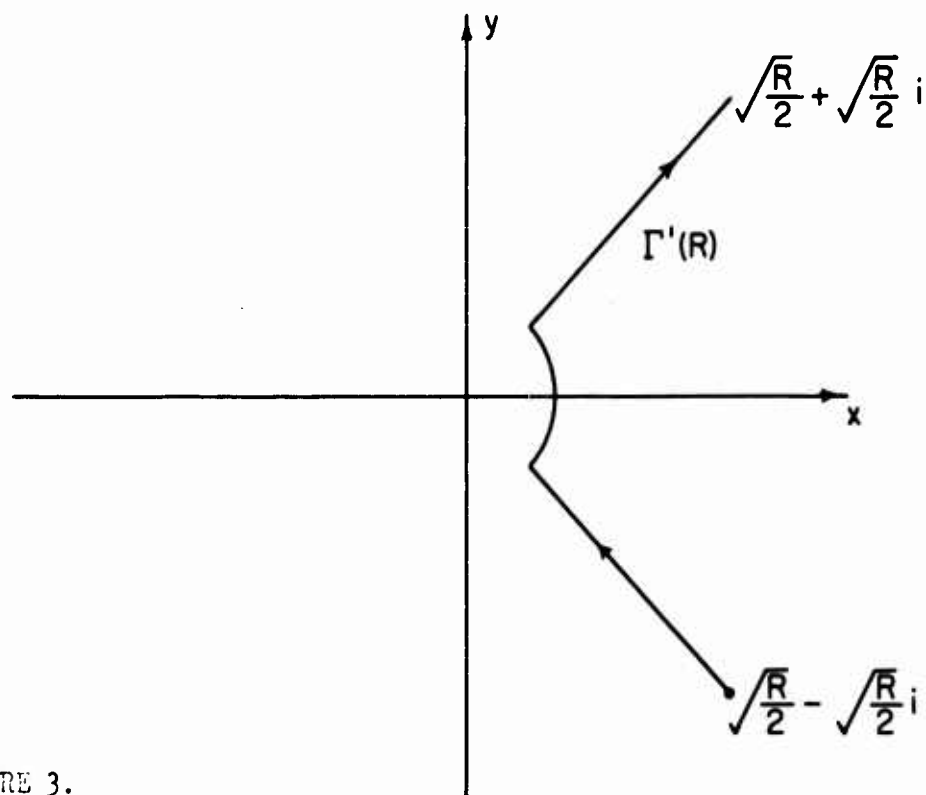


FIGURE 3.

This contour consists of parts of the lines  $y = x$  and  $y = -x$  and one-fourth of the unit circle with center at the origin. Thus

$$\int_{\Gamma(R)} \frac{\exp(\lambda - \xi \sqrt{\mu^2 + \lambda}) d\lambda}{(\mu^2 + \lambda)(\Delta \mu^2 + \frac{1}{\alpha} \sqrt{\mu^2 + \lambda} + \lambda)} = \frac{2 \exp(-\mu^2)}{(\Delta - 1)} \int_{\Gamma'(R)} \frac{\exp(v^2 - v\xi) dv}{(\mu^2 + \frac{1}{\beta} v + \frac{v^2}{\Delta - 1})v}$$

where  $\beta = (\Delta - 1)\alpha$  as before.

Since the integrand

$$\frac{\exp(v^2 - v\xi)}{(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1})v}$$

is analytic for all  $v$  in the half plane  $x > 0$ ,  $\Gamma'(R)$  can be replaced by the contour  $\Gamma''(S)$  shown in Figure 4, where  $S = \frac{R}{2}$ .

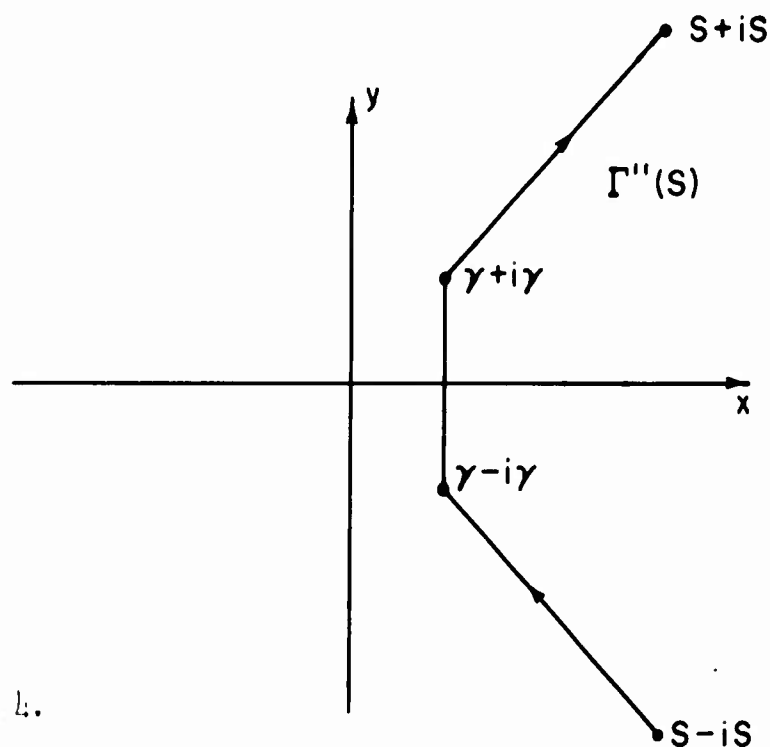


FIGURE 4.

This gives the following expression for  $C_2$

$$C_2 = \frac{2}{\pi^2 i} \int_0^\infty \mu \exp(-\mu^2) \sin(\mu\eta) d\mu \left[ \lim_{S \rightarrow \infty} \int_{\Gamma''(S)} \frac{\exp(v^2 - v\xi) dv}{\left( \mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1} \right) v} \right].$$

Along the contour  $\Gamma''(S)$  the following substitutions are valid:

$$\mu \sin(\mu\eta) = -\frac{\partial}{\partial\eta} \cos(\mu\eta), \quad \frac{\exp(-v\xi)}{v} = \int_{\xi}^{\infty} \exp(-v\xi') d\xi'$$

(because  $\operatorname{Re}(v) > 0$  on  $\Gamma''(S)$ ), and

$$\frac{1}{\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}} = \exp\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right) \int_1^{\infty} \exp\left[-\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right)\sigma\right] d\sigma.$$

(because  $\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}$  has positive real part along  $\Gamma''(S)$ ).

Applying these substitutions to  $C_2$  gives

$$C_2 = -\frac{2}{\pi^2 i} \frac{\partial}{\partial\eta} \int_0^{\infty} \cos(\mu\eta) d\mu \left[ \lim_{S \rightarrow \infty} (Q) \right]$$

where

$$Q = \int_{\Gamma''(S)} dv \int_1^{\infty} \exp(-\mu^2\sigma) d\sigma \int_{\xi}^{\infty} \exp\left[\frac{\Delta-\sigma}{\Delta-1} v^2 - v\left(\xi' + \frac{\sigma-1}{\beta}\right) d\xi'\right].$$

The limit of  $Q$  as  $S \rightarrow \infty$  is actually an improper real integral. Therefore it is permissible to interchange this limit process with the various integrations to get

$$C_2 = -\frac{2}{\pi^2 i} \frac{\partial}{\partial\eta} \int_{\xi}^{\infty} d\xi' \int_1^{\infty} d\sigma \int_0^{\infty} \cos(\mu\eta) \exp(-\mu^2\sigma) d\mu \left[ \lim_{S \rightarrow \infty} \int_{\Gamma''(S)} \exp \frac{\Delta-\sigma}{\Delta-1} v^2 \left( \xi' + \frac{\sigma-1}{\beta} \right) dv \right].$$

The last integration must be divided into two cases. The case where  $\sigma > \Delta$  gives an integral of the form

$$\lim_{S \rightarrow \infty} \int_{\Gamma''(S)} \exp(-Fv^2 - Gv) dv$$

where  $F$  and  $G$  are positive real numbers. The integrand is analytic for all values of  $v$ . Therefore the integral around a closed path is zero. If  $\Gamma''(S)$  is closed by the vertical line from  $S + iS$  to  $S - iS$  one obtains the contour shown in Figure 5.

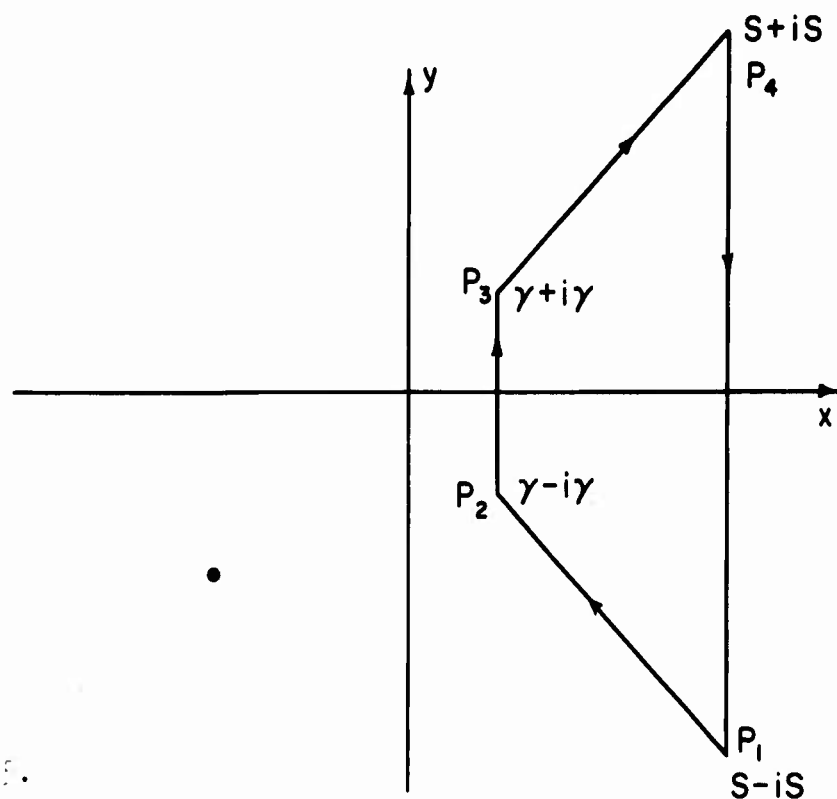


Figure 1.

Along the line segment  $P_4P_1$ ,  $v = S + iy$  where  $-S \leq y \leq S$ . For these values of  $v$

$$|\exp(-Fv^2 - Gv)| = \exp\left[-F(S^2 - y^2) - GS\right] \leq \exp(-GS).$$

This gives

$$\left| \int_{P_4P_1} \exp(-Fv^2 - Gv) dv \right| \leq 2S \exp(-GS),$$

and this goes to zero as  $S \rightarrow \infty$ . Thus

$$\lim_{S \rightarrow \infty} \int_{\Gamma'(S)} \exp(-Fv^2 - Gv) dv = 0.$$



The case where  $\sigma < \Delta$  gives an integral of the form

$$\lim_{S \rightarrow \infty} \int_{\Gamma''(S)} \exp(Jv^2 - Kv) dv$$

where  $J$  and  $K$  are positive real numbers. This will be shown to be equal to

$$\lim_{S \rightarrow \infty} \int_{\gamma - iS}^{\gamma + iS} \exp(Jv^2 - Kv) dv .$$

To do this it must be observed that

$$\int_{\Gamma''(S)} \exp(Jv^2 - Kv) dv$$

differs from

$$\int_{\gamma - iS}^{\gamma + iS} \exp(Jv^2 - Kv) dv$$

by the contribution from the horizontal segments  $P_4P_5$  and  $P_6P_1$  shown in Figure 6.

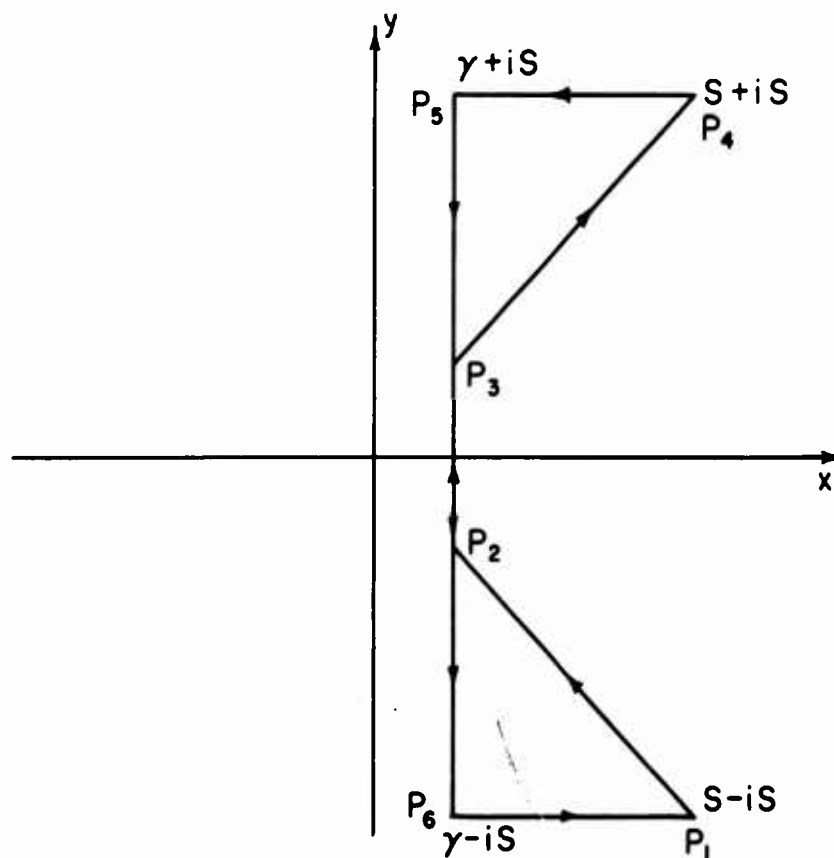


FIGURE 6.

For the integral along the segment  $P_4P_5$ ,  $v = x + iS$  where  $\gamma \leq x \leq S$ .  
When  $v$  is on the segment of this line where  $\gamma \leq x \leq S/2$ ,

$$|\exp(Jv^2 - Kv)| = \exp[J(x^2 - S^2) - Kx] \leq \exp\left[J\left(\frac{S^2}{4} - S^2\right)\right] = \exp\left(-\frac{3JS^2}{4}\right).$$

When  $v$  is on the segment of  $P_4P_5$  where  $S/2 \leq x \leq S$ ,

$$|\exp(Jv^2 - Kv)| = \exp[J(x^2 - S^2) - Kx] \leq \exp\left(-\frac{KS}{2}\right).$$

Therefore

$$\left| \int_{P_4P_5} \exp(Jv^2 - Kv) dv \right| \leq S \left( \exp\left(-\frac{3JS^2}{4}\right) + \exp\left(-\frac{KS}{2}\right) \right),$$

and this goes to zero as  $S \rightarrow \infty$ .

This now leaves for  $C_2$  the expression

$$C_2 = -\frac{2}{\pi^2 i} \frac{\partial}{\partial \eta} \int_{\xi}^{\infty} d\xi' \int_1^{\Delta} d\sigma \int_0^{\infty} \cos(\mu\eta) \exp(-\mu^2\sigma) Q d\mu, \quad (21)$$

where

$$Q = \lim_{S \rightarrow \infty} \int_{\gamma - iS}^{\gamma + iS} \exp\left[\frac{\Delta - \sigma}{A-1} v^2 - v\left(\xi' + \frac{\sigma-1}{\beta}\right)\right] dv.$$

Let  $v$  be written  $\gamma + iy$  for the evaluation of  $Q$ . Then  $dv = i dy$  and

$$\begin{aligned} & \int_{\gamma - iS}^{\gamma + iS} \exp(Av^2 - Bv) dv \\ &= i \int_{-S}^S \exp\left[A(\gamma^2 - y^2 + 2\gamma yi) - B(\gamma + iy)\right] dy \\ &= i \exp(A\gamma^2 - B\gamma) \int_{-S}^S \exp(-Ay^2) \cos\left[(2A\gamma - B)y\right] dy \end{aligned}$$

$$= 2i \exp(A\gamma^2 - B\gamma) \int_0^S \exp(-A\gamma^2) \cos[(2A\gamma - B)\gamma] d\gamma.$$

As  $S \rightarrow \infty$  this last expression approaches

$$Q = 2i \exp(A\gamma^2 - B\gamma) \frac{\sqrt{\pi}}{2\sqrt{A}} \exp\left[-\frac{4A^2\gamma^2 - 4AB\gamma + B^2}{4A}\right] = \frac{i\sqrt{\pi}}{\sqrt{A}} \exp\left[-\frac{B^2}{4A}\right].$$

Putting in  $A = \frac{\Delta-\sigma}{\Delta-1}$  and  $B = \xi' + \frac{\sigma-1}{\beta}$  gives

$$Q = i\sqrt{\pi} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \exp\left[-\frac{1}{4} \frac{\Delta-1}{\Delta-\sigma} \left(\xi' + \frac{\sigma-1}{\beta}\right)^2\right].$$

Since  $Q$  does not involve  $\mu$ , the third integration in formula (21) can be done separately

$$\int_0^\infty \cos(\mu\eta) \exp(-\mu^2\sigma) d\mu = \frac{\sqrt{\pi}}{2\sqrt{\sigma}} \exp\left[-\frac{\eta^2}{4\sigma}\right]. \quad (22)$$

The integration on  $\xi'$  can be performed separately by observing that  $Q$  is the only factor involving  $\xi'$ .

$$\int_{\xi}^{\infty} Q d\xi' = i\sqrt{\pi} \int_{\xi}^{\infty} \exp\left[-\frac{1}{4} \frac{\Delta-1}{\Delta-\sigma} \left(\xi' + \frac{\sigma-1}{\beta}\right)^2\right] \sqrt{\frac{\Delta-1}{\Delta-\sigma}} d\xi'.$$

Substituting  $z = \frac{1}{2} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi' + \frac{\sigma-1}{\beta}\right)$  gives  $dz = \frac{1}{2} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} d\xi'$

$$\text{and } \int_{\xi}^{\infty} Q d\xi' = 2i\sqrt{\pi} \int_{\frac{1}{2}\sqrt{\frac{\Delta-1}{\Delta-\sigma}}\left(\xi + \frac{\sigma-1}{\beta}\right)}^{\infty} \exp(-z^2) dz = \pi i \operatorname{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi + \frac{\sigma-1}{\beta}\right)\right]. \quad (23)$$

Combining formulas (22) and (23) with (21) gives

$$\begin{aligned} C_2 &= -\frac{1}{\sqrt{\pi}} \frac{\partial}{\partial \eta} \int_1^{\Delta} \frac{1}{\sqrt{\sigma}} \exp\left[-\frac{\eta^2}{4\sigma}\right] \operatorname{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi + \frac{\sigma-1}{\beta}\right)\right] d\sigma \\ &= \frac{\eta}{2\sqrt{\pi}} \int_1^{\Delta} \sigma^{-3/2} \exp\left[-\frac{\eta^2}{4\sigma}\right] \operatorname{erfc}\left[\frac{1}{2} \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\xi + \frac{\sigma-1}{\beta}\right)\right] d\sigma. \end{aligned} \quad (24)$$

This gives the final solution

$$C = C_1 + C_2 \quad (25)$$

where

$$C_1 = \operatorname{erfc} \frac{\eta}{2}.$$

### Discussion of Inversion Formulas

In the half plane  $\operatorname{Re}(\lambda) \geq 0$  both  $\psi_1 = \frac{\mu}{\lambda(\mu^2 + \frac{\lambda}{D})}$  and

$$\psi_2 = \frac{(\frac{D}{D'} - 1)\mu \exp[-\sqrt{\mu^2 + \frac{\lambda}{D}}(x-a)]}{(\mu^2 + \frac{\lambda}{D}) (D' \mu^2 + \frac{D}{a}\sqrt{\mu^2 + \frac{\lambda}{D}} + \lambda)}$$

are of order  $1/\lambda^2$ . When the real part of  $\lambda$  is not negative,  $|D\mu^2 + \lambda| \geq |\lambda|$  and  $|\psi_1 \lambda^2| \leq D|\mu|$ . Similarly when  $\operatorname{Re}(\lambda) \geq 0$ ,  $|D' \mu^2 + \frac{D}{a}\sqrt{\mu^2 + \frac{\lambda}{D}} + \lambda| \geq |\lambda|$  because  $\frac{D}{a}\sqrt{\mu^2 + \frac{\lambda}{D}}$  has its real and imaginary parts the same sign as those of  $\lambda$ . Thus

$$|\psi_2 \lambda^2| \leq \left(\frac{D'}{D} - 1\right) D|\mu|.$$

When  $\operatorname{Re}(\lambda) > 0$  both  $\psi_1$  and  $\psi_2$  are analytic functions of  $\lambda$  and are both real if  $\lambda$  is real. Therefore by a theorem in Churchill<sup>(6)</sup> the inverse of  $\psi_1 = \psi_1 + \psi_2$  is given by the formula

$$\theta(x, \mu, t) = \frac{1}{2\pi i} \lim_{R \rightarrow \infty} \int_{\gamma - iR}^{\gamma + iR} \psi \exp(\lambda t) d\lambda,$$

for  $\gamma > 0$ , and is independent of  $\gamma$ .

It was shown before that  $\int_0^\infty C(x, y, t) dy$  exists. Therefore since

$C(x, y, t)$  is assumed to be a continuous differentiable function of  $y$ , one can write<sup>(7)</sup>

$$C(x, y, t) = \frac{2}{\pi} \int_0^\infty \sin(\mu y) d\mu \int_0^\infty C(x, y', t) \sin(\mu y') dy' = \frac{2}{\pi} \int_0^\infty \sin(\mu y) \theta(x, \mu, t) d\mu.$$

Let  $C(x,y,t)$  be a solution. Then  $\theta(x,\mu,t)$  and  $\psi(x,\mu,\lambda)$ , determined by  $C(x,y,t)$ , must exist.  $\psi(x,\mu,\lambda)$  is then uniquely determined and uniquely inverted to  $\theta(x,\mu,t)$ . But  $\theta(x,\mu,t)$  has a unique inverse also hence there is only one possible choice for  $C(x,y,t)$ .

### FISHER'S SOLUTION

#### Statement of the Problem

The idealized situation studied by Fisher<sup>(2)</sup> is the same as that of Whipple. The half space,  $y > 0$ , is filled with a material of diffusivity  $D$  except for a thin slab of width  $\delta$ . This slab is bounded by the planes  $x = 0$  and  $x = -\delta$ . The diffusivity in this slab is  $D'$  ( $D' \gg D$ ). At time  $t = 0$  the concentration on the surface  $y = 0$  is suddenly raised to unity and maintained at unity. The problem is to find  $C = C(x,y,t)$  elsewhere. Fisher refers to the plane  $y = 0$  as the free surface.

The diffusion equation holds for the concentration  $C$  outside the thin slab. That is

$$D \nabla^2 C = \frac{\partial C}{\partial t}, \quad (26)$$

for  $C$  outside the thin slab.

#### The Differential Equation in the Slab

Let the thickness of the slab,  $\delta$ , be very small so that variations in  $C$  across it are negligible. Consider a rectangular parallelepiped in the slab of length  $\Delta z$  in the  $z$ -direction, of width  $\Delta y$  in the  $y$ -direction and of width slightly greater than  $\delta$  in the  $x$ -direction. Let this be oriented in the slab with two of its faces just outside the slab and parallel to the slab. Let  $P$  be the point at the center of this parallelepiped. Let  $\partial C / \partial t$ , denote the value of that derivative at the point  $P$ . Then the flow of material into this volume is approximately  $\delta(\Delta y)(\Delta z) \partial C / \partial t$ .

This can also be written as the sum of the flow through the sides of the parallelepiped. In the  $z$ -direction there is no flow. In the  $x$ -direction there is the flow  $F_x$  just outside the surface  $x = 0$  (and its negative just outside the surface  $x = -\delta$ ). Therefore the amount of material coming into the volume in the  $x$ -direction is

$$-2(F_x)_0 (\Delta y) (\Delta z),$$

where the subscript zero indicates that  $F_x$  is evaluated just outside the slab. Of course by Fick's law (outside the slab)

$$(F_x)_0 = -D \left( \frac{\partial C}{\partial x} \right)_0.$$

The flow at the point P in the y-direction is  $F_y$  and so the amount of material coming into the volume in the y-direction is

$$\left(F_y - \frac{\partial F_y}{\partial y} \frac{\Delta y}{2}\right) (\Delta z) \delta - \left(F_y + \frac{\partial F_y}{\partial y} \frac{\Delta y}{2}\right) (\Delta z) \delta = - \frac{\partial F_y}{\partial y} (\Delta y) (\Delta z) \delta.$$

Noting that inside the slab  $F_y = -D' \frac{\partial C}{\partial y}$  and equating the expressions for the amount of material flowing into the volume gives

$$-2(F_x)_0 (\Delta y) (\Delta z) - \frac{\partial F_y}{\partial y} (\Delta y) (\Delta z) \delta = \frac{\partial C}{\partial t} (\Delta y) (\Delta z) \delta$$

or

$$\frac{2D}{\delta} \left(\frac{\partial C}{\partial x}\right)_0 + D' \frac{\partial^2 C}{\partial y^2} = \frac{\partial C}{\partial t} \quad (27)$$

for the concentration in the slab.

#### Fisher's Approximate Solution

At this stage the problem is identical to that solved by Whipple. Equations (26) and (27) are just the same as Eqs. (2) and (11).

Equation (26) is simplified by the observation that the concentration of the diffusing material will be much greater in the slab than outside because of the much higher diffusivity inside. This means that near the surface  $x = 0$  and far from the surface  $y = 0$  the flow of material is normal to the surface  $x = 0$ .

In terms of the parameters of the problem this says that

$$\left|\frac{\partial C}{\partial y}\right| \ll \left|\frac{\partial C}{\partial x}\right|.$$

From this it is concluded that

$$\left|\frac{\partial^2 C}{\partial y^2}\right| \ll \left|\frac{\partial^2 C}{\partial x^2}\right|.$$

Equation (26) is therefore reduced to

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad (28)$$

for points outside the slab.

Let the following substitutions be made:

$$t_1 = \frac{Dt}{\delta^2}, \quad x_1 = \frac{x}{\delta}, \quad y_1 = \frac{y}{\delta \left(\frac{D}{\delta}\right)^{1/2}}.$$

Equation (28), written in terms of these dimensionless parameters, becomes

$$\frac{\partial^2 C}{\partial x_1^2} = \frac{\partial C}{\partial t_1} \quad (29)$$

for points outside the slab and Eq. (27) becomes

$$2 \left( \frac{\partial C}{\partial x_1} \right)_0 + \frac{\partial^2 C}{\partial y_1^2} = \frac{\partial C}{\partial t_1} \quad (30)$$

for points in the slab.

Fisher solves these two equations by a numerical method and uses the numerical solution to draw some conclusions about  $C(x, y, t)$ . He observes that  $C$  rises in the slab at a rapidly decreasing rate. Because of this the value of  $C$  outside the slab can be treated as though the value of  $C$  in the slab is independent of the time. Let  $\phi(y_1, t_1)$  be the concentration in the slab.

The assumption that  $\phi(y_1, t_1)$  is independent of the time gives for a solution of Eq. (29)

$$C = \phi(y_1, t_1) \operatorname{erfc} \left( \frac{x_1}{2\sqrt{t_1}} \right), \quad (31)$$

and this takes on the value  $\phi(y_1, t_1)$  when  $x_1 = 0$ .

At this point Fisher's reasoning is difficult to follow. He says that  $\frac{\partial C}{\partial t}$  in the slab  $\gg \left( \frac{\partial C}{\partial t} \right)_{\max}$  outside the slab for most of the time. From this he concludes that the value of  $\phi(y_1, t_1)$  can be derived approximately from Eq. (30) by assuming  $\frac{\partial C}{\partial t_1} = 0$ .

This assumption applied to Eq. (30) is that

$$2 \left( \frac{\partial C}{\partial x_1} \right)_0 + \frac{\partial^2 \phi}{\partial y_1^2} = 0. \quad (32)$$

However

$$\frac{\partial C}{\partial x_1} = - \frac{1}{\sqrt{\pi t_1}} \phi(y_1, t_1) \exp \left( - \frac{x_1^2}{4t_1} \right)$$

for points outside the slab, therefore

$$\left(\frac{\partial C}{\partial x_1}\right)_0 = -\frac{1}{\sqrt{\pi t_1}} \phi(y_1, t_1) .$$

Putting this last expression into Eq. (32) gives

$$-\frac{2\phi}{\sqrt{\pi t_1}} + \frac{\partial^2 \phi}{\partial y_1^2} = 0 ,$$

which is essentially an ordinary differential equation.

The solution to Eq. (33) which is bounded in  $y_1$  and satisfies the condition that  $C = 1$  when  $y_1 = 0$  is

$$\phi(y_1, t_1) = \exp \left( -\frac{\sqrt{2} y_1}{\pi^{1/4} t_1^{1/4}} \right) .$$

This gives the final formula for  $C$ .

$$C = \exp \left( -\frac{\sqrt{2} y_1}{\pi^{1/4} t_1^{1/4}} \right) \operatorname{erfc} \left( \frac{x_1}{2\sqrt{t_1}} \right) ,$$

or in terms of  $x$ ,  $y$ , and  $t$

$$C = \exp \left( -\frac{\sqrt{2} y}{\sqrt{\delta} \sqrt{\frac{D}{D}} (\pi D t)^{1/4}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{D t}} \right) \quad (34)$$

#### DISCUSSION OF VALIDITY OF FORMULAS

The solution derived by Whipple, Eq. (25), is the exact solution to the diffusion equation with the approximate boundary condition Eq. (11), the boundary conditions Eqs. (4), (5), (6), and the conditions that  $\frac{\partial C}{\partial y}$  and  $C$  both go to zero as  $y \rightarrow \infty$ . His solution has the disadvantage of being a numerical integration.

Fishers' formula, Eq. (34), on the other hand, is ideal for computation if it is correct. The reasoning of Fisher will now be discussed.

First the simplification of the diffusion equation to the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (35)$$



would have to be verified. This can be checked by using the exact solution of Whipple and comparing  $\partial^2 C / \partial x^2$  and  $\partial^2 C / \partial y^2$ . If, as seems not unlikely,  $\partial^2 C / \partial y^2$  is negligible compared to  $\partial^2 C / \partial x^2$  for values of  $x$  and  $y$  of interest, then the concentration in that region would satisfy Eq. (35).

The next step is difficult to check. Fisher concludes that  $\phi(y_1, t_1)$  is a slowly varying function of time and therefore

$$C = \phi(y_1, t_1) \operatorname{erfc} \left( \frac{x_1}{2\sqrt{t_1}} \right)$$

(where  $\phi$  is still an unknown function) satisfies the equation

$$\frac{\partial C}{\partial t_1} = \frac{\partial^2 C}{\partial x_1^2}.$$

This is true if

$$\frac{\partial \phi}{\partial t_1} \operatorname{erfc} \left( \frac{x_1}{2\sqrt{t_1}} \right)$$

is small compared to

$$\frac{x_1}{2\sqrt{\pi t_1}} \phi \exp \left( -\frac{x_1^2}{4t_1} \right).$$

The only way to verify this seems to be to look at Fisher's final solution and determine if this is so.

One observation seems pertinent here. If the diffusion equation can be reduced to Eq. (35) then this last step is a necessary condition for Fisher's solution to be a solution to the diffusion differential Eq. (26). If, on the other hand, Eq. (35) is not valid, then Fisher's solution might still be a good approximate solution even if this last test fails.

The next step is again one which can be checked by means of Whipple's solution. Fisher uses the equation in the slab.

$$2 \left( \frac{\partial C}{\partial x_1} \right)_0 + \frac{\partial^2 \phi}{\partial y_1^2} = 0 \quad (36)$$

to determine  $\phi(y_1, t_1)$ . This requires that  $\partial C / \partial t_1$  in the slab be small compared

to  $2(\partial C/\partial x_1)_0$ . Since Fisher's solution satisfies Eq. (36) exactly, this last condition is a necessary one for it to satisfy the boundary condition Eq. (27).

#### DISCUSSION OF BORISOV, GOLIKOV AND LJUBOV'S WORK

The following is a partial study of the derivation of Fisher's solution from that of Whipple's by Borisov et al.<sup>(4)</sup>

Consider the formula given by Whipple for the concentration  $C$  in the grain volume:

$$C = C_1 + C_2$$

where

$$C_1 = \frac{2}{\pi} \int_0^\infty \left[ 1 - \exp(-\mu^2) \right] \sin(\mu\eta) \frac{d\mu}{\mu}$$

and

$$C_2 = \frac{2}{\pi^2 i} \int_0^\infty \mu \exp(-\mu^2) \sin(\mu^2) d\mu \left[ \lim_{S \rightarrow \infty} \int_{\Gamma''(S)} \frac{\exp(v^2 - v\xi) dv}{\left( \mu^2 + \frac{v}{\beta} + \frac{v^2}{A-1} \right)^{1/2}} \right].$$

It should be noted that in the convention used by the Borisov et al.  $\eta = \frac{y}{\sqrt{Dt}}$ , as in Whipple's paper, but  $\xi = \frac{x}{\sqrt{Dt}}$  where  $x$  is the distance measured from the grain boundary. (Whipple has  $\xi = \frac{x-a}{\sqrt{Dt}}$ .) All other symbols in  $C_1$  and  $C_2$  are the same as in Whipple's paper.

The above expression is, of course, not the final form of Whipple's section.

It is desired to evaluate the contour integral of  $C_2$  along the  $y$ -axis instead of  $\Gamma''(S)$ . More precisely, let  $\Gamma(S, \epsilon)$  be the contour which consists of the part of the  $y$ -axis between the points  $-iS$  and  $iS$  excluding the segment between  $-i\epsilon$  and  $i\epsilon$ . (It is assumed that  $S$  is a very large positive real number while  $\epsilon$  is a very small positive real number.) The remaining part of  $\Gamma(S, \epsilon)$  will be the half of the circle  $v = \epsilon e^{i\theta}$  which is to the right of the  $y$ -axis. This contour is shown in Figure 7.

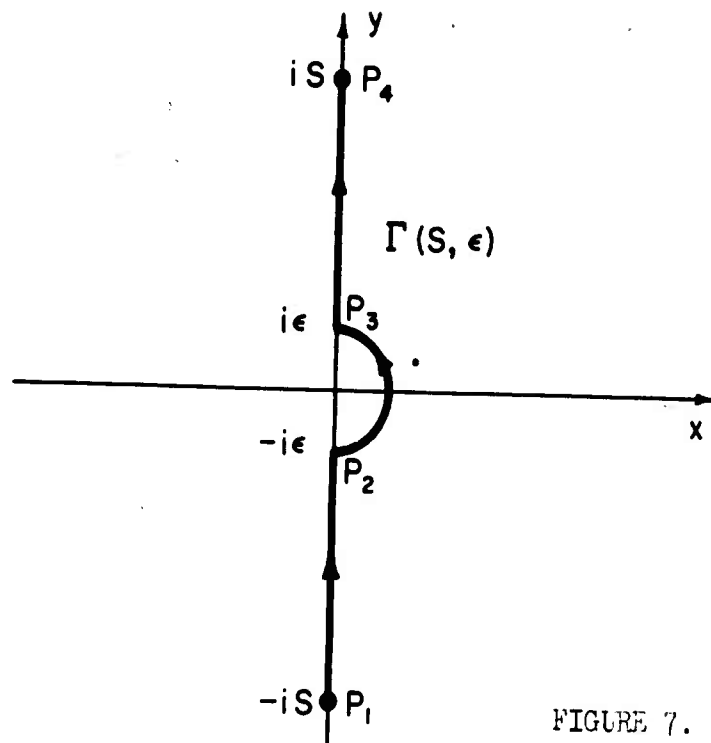


FIGURE 7.

It should be noted that the  $x$  and  $y$  of Figure 7 and the  $y$  to be used as a variable of integration on contour are not the original  $x$  and  $y$  of the problem.

Let  $f(v) = \frac{\exp(v^2 - v\xi)}{\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right)v}$ . The function  $f(v)$  is analytic on

$\Gamma(S, \epsilon)$  and at all points to the right of  $\Gamma(S, \epsilon)$ . This is because the zeros of  $\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}$  are all to the left of the  $y$ -axis except for the possibility  $v = 0$ .  $f(v)$  is bounded by  $\exp(v^2 - v\xi)$  as  $v \rightarrow \infty$ . Therefore by an argument very much

like that used just before Eq. (21) it can be concluded that

$$\lim_{S \rightarrow \infty} \int_{\Gamma(S, \epsilon)} \frac{\exp(v^2 - v\xi) dv}{\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right)v} = \lim_{S \rightarrow \infty} \int \frac{\exp(v^2 - v\xi) dv}{\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right)v}.$$

Therefore it is required to evaluate

$$\int_{\Gamma(S, \epsilon)} \frac{\exp(v^2 - v\xi) dv}{\left(\mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1}\right)v}.$$

This integral is clearly independent of  $\epsilon$  and so it is permissible to find the limit as  $\epsilon \rightarrow \infty$ .

First on the section of  $\Gamma(S, \epsilon)$  which consists of the half circle  $v = \epsilon e^{i\theta}$ ,  $-\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2}$ , the integral becomes

$$i \int_{-\pi/2}^{\pi/2} \frac{\exp(\epsilon^2 e^{2i\theta} - \xi \epsilon e^{i\theta}) d\theta}{\left(\mu^2 + \frac{\epsilon e^{i\theta}}{\beta} + \frac{\epsilon^2 e^{2i\theta}}{\Delta-1}\right)}.$$

As  $\epsilon \rightarrow 0$  this integrand approaches  $1/\mu^2$  uniformly in  $\theta$ , therefore the integral approaches

$$i \int_{-\pi/2}^{\pi/2} \frac{d\theta}{\mu^2} = \frac{i\pi}{\mu^2} \text{ as } \epsilon \rightarrow 0.$$

For the section of  $\Gamma(S, \epsilon)$  which lies along the y-axis the substitution  $v = iy$  is made. On this section the integral becomes

$$\int_{-S}^{-\epsilon} \frac{\exp(-y^2 - \xi y i)}{\left(\mu^2 - \frac{y^2}{\Delta-1} + \frac{iy}{\beta}\right)} \frac{dy}{y} + \int_{\epsilon}^S \frac{\exp(-y^2 - \xi y i)}{\left(\mu^2 - \frac{y^2}{\Delta-1} + \frac{iy}{\beta}\right)} \frac{dy}{y}.$$

If  $y$  is replaced by  $-y$  in the first integral one obtains

$$\int_{\epsilon}^S \frac{\exp(-y^2 - \xi y i)}{\left(\mu^2 - \frac{y^2}{\Delta-1} + \frac{iy}{\beta}\right)} - \frac{\exp(-y^2 + \xi y i)}{\left(\mu^2 - \frac{y^2}{\Delta-1} - \frac{iy}{\beta}\right)} \frac{dy}{y}$$

$$= 2i \int_{\epsilon}^S \exp(-y^2) \left[ \frac{\left( \frac{y^2}{\Delta-1} - \mu^2 \right) \sin(\xi y) - \frac{y}{\beta} \cos \xi y}{\left( \frac{y^2}{\Delta-1} - \mu^2 \right) + \frac{y^2}{\beta^2}} \right] \frac{dy}{y}.$$

In this form it is clear that there is a limit as  $\epsilon \rightarrow 0$  and this limit is

$$2i\theta a \int_0^S \exp(-y^2) \left[ \frac{a(y^2 - \mu^2\theta) \sin \xi y - y\sqrt{Dt} \cos(\xi y)}{a^2(y^2 - \mu^2\theta)^2 + y^2 Dt} \right] \frac{dy}{y}$$

where  $\theta = \Delta-1$  and  $\beta = \theta a / \sqrt{Dt}$ . This now permits one to write

$$\int_{\Gamma(S, \epsilon)} \frac{\exp(v^2 - \xi v)}{\left( \mu^2 + \frac{v}{\beta} + \frac{v^2}{\Delta-1} \right)} \frac{dv}{v}$$

$$= \frac{i\pi}{\mu^2} + 2i\theta a \int_0^S \exp(-y^2) \left[ \frac{a(y^2 - \mu^2\theta) \sin(\xi y) - y\sqrt{Dt} \cos \xi y}{a^2(y^2 - \mu^2\theta)^2 + y^2 Dt} \right] \frac{dy}{y}.$$

Now when this last expression is put into the expression for  $C_2$  one gets for the concentration  $C$

$$C = \frac{2}{\pi} \int_0^{\infty} \sin(\mu \eta) \frac{d\mu}{\mu}$$

$$+ \frac{4\theta a}{\pi^2} \int_0^{\infty} \mu \sin(\mu \eta) \exp(-\mu^2) d\mu \int_0^{\infty} \exp(-y^2) \left[ \frac{a(y^2 - \mu^2\theta) \sin(\xi y) - y\sqrt{Dt} \cos(\xi y)}{a^2(y^2 - \mu^2\theta)^2 + y^2 Dt} \right] \frac{dy}{y}.$$

The next step is to evaluate the first integral and to replace  $\mu$  by  $\xi$ ,  $y$  by  $\mu$ ,  $\eta$  by  $y/\sqrt{Dt}$  and  $\xi$  by  $x/\sqrt{Dt}$  in the double integral. Then

$$C = 1 + \frac{4a\theta}{\pi^2} \int_0^{\infty} \xi \exp(-\xi^2) \sin\left(\frac{\xi y}{\sqrt{Dt}}\right) d\xi \int_0^{\infty} \exp(-\mu^2) \left[ \frac{a(\mu^2 - \xi^2\theta) \sin\left(\frac{\mu x}{\sqrt{Dt}}\right) - \mu\sqrt{Dt} \cos\left(\frac{\mu x}{\sqrt{Dt}}\right)}{\mu^2 Dt + a^2(\mu^2 - \xi^2\theta)^2} \right] \frac{d\mu}{\mu}.$$

The substitution  $\xi' = \xi/\sqrt{Dt}$  and  $\mu' = \mu/\sqrt{Dt}$  gives for C, after removing the primes,

$$C = 1 + \frac{4a\theta}{\pi^2} X$$

$$\int_0^\infty \xi \sin(\xi y) d\xi \int_0^\infty \exp \left[ -(\xi^2 + \mu^2)Dt \right] \left[ \frac{a(\mu^2 - \xi^2\theta) \sin(\mu x) - \mu \cos(\mu x)}{\mu^2 + a^2(\mu^2 - \xi^2\theta)^2} \right] \frac{d\mu}{\mu} . \quad (37)$$

This appears to be Eq. (1.9) in the paper by Borisov et al.<sup>(4)</sup>

The following formula is given as a consequence of Eq. (37) with some negligible quantities neglected.

$$C = 1 - \frac{2}{\pi^2} X$$

$$\int_0^\infty \int_0^\infty \frac{z \sin(\eta r) + \cos(\eta r)}{(1 + z^2)\eta} \sin \left[ (z\eta)^{1/2} u \right] \exp(-\eta^2 - \eta z \varepsilon) d\eta dz, \quad (38)$$

where

$$r = \frac{x}{\sqrt{Dt}}, \quad u = \frac{y}{(Dt)^{1/2} \sqrt{a\theta}}, \quad \varepsilon = \frac{\sqrt{Dt}}{a\theta}.$$

The substitutions

$$z = a \left( \frac{\xi^2\theta}{\mu} - \mu \right) \text{ and } \eta = \mu(Dt)^{1/2}$$

seem to be the ones used to get Eq. (38).

With these substitutions the integrand in Eq. (37) becomes

$$- \frac{\xi \sqrt{Dt}}{\mu} \sin \left[ \sqrt{\frac{\eta^2}{\theta Dt} + \frac{z\eta}{\theta a \sqrt{Dt}}} y \right] \exp \left( -\eta^2 - \frac{\eta^2}{\theta} - \frac{z\eta \sqrt{Dt}}{\theta a} \right) \frac{z \sin(\eta r) + \cos(\eta r)}{(1 + z^2)\eta}$$

where the  $\frac{\xi \sqrt{Dt}}{\mu}$  is left in that form so that the Jacobian will cancel it. Since

$$\begin{aligned} \frac{\partial z}{\partial \xi} &= \frac{2a\theta\xi}{\mu} & \frac{\partial z}{\partial \mu} &= -\frac{a\xi^2\theta}{\mu^2} - a \\ \frac{\partial \eta}{\partial \xi} &= 0 & \frac{\partial \eta}{\partial \mu} &= Dt \end{aligned}$$

the Jacobian of the transformations is  $\mu/2a\theta\xi\sqrt{Dt}$  the reciprocal of the determinant

$$\begin{vmatrix} \frac{\partial z}{\partial \xi} & \frac{\partial z}{\partial \mu} \\ \frac{\partial \eta}{\partial \xi} & \frac{\partial \eta}{\partial \mu} \end{vmatrix}.$$

With this Eq. (37) can be written

$$C = 1 - \frac{2}{\pi^2} \times$$

$$\int_0^\infty \int_{a\eta/\sqrt{Dt}}^\infty \sin\left(\sqrt{\frac{\eta^2}{\theta Dt} + \frac{z\eta}{\theta a \sqrt{Dt}}} y\right) \exp\left(-\eta^2 - \frac{\eta^2}{\theta} - z\eta\epsilon \frac{z \sin(r\eta) + \cos r\eta}{(1+z^2)\eta}\right) dz d\eta. \quad (39)$$

Writing this again in a clearer form

$$C = 1 - \frac{2}{\pi^2} \times$$

$$\int_0^\infty \int_{a\eta/\sqrt{Dt}}^\infty \sin\left(\sqrt{\frac{\eta^2}{\theta Dt} + \frac{z\eta}{\theta a \sqrt{Dt}}} y\right) \exp\left(-\eta^2 - \frac{\eta^2}{\theta} - z\eta\epsilon \left[ \frac{z \sin(r\eta) + \cos(r\eta)}{(1+z^2)\eta} \right]\right) dz d\eta.$$

This reduces to Eq. (2.2) of Borisov et al.<sup>(4)</sup> if the term  $\eta^2/\theta Dt$  can be ignored compared to  $z\eta/\theta a \sqrt{Dt}$  and if the lower limit on the integration on  $z$  can be replaced by 0. The approximation  $-\eta^2 - \eta^2/\theta = -\eta^2$  is always good since  $\theta$  is so large.

## CONCLUSIONS AND RECOMMENDATIONS

The three major published works on grain-boundary diffusion have been considered and the following conclusions reached. Whipple's solution is exact. The solution obtained by Borisov et al. is equivalent to that obtained by Whipple. The relationship of Fisher's approximation to Whipple's solution has been examined but no conclusion about its validity has been reached. At least one very weak point in Fisher's argument has been found.

Having proceeded this far one may recognize rather sharply several specific problems that could very profitably be considered. Several of these are enumerated below.

- (1) Numerical Evaluation of Whipple's Solution. With the sure knowledge that Whipple's solution is exact it seems appropriate to inquire how well this solution describes experimental results. The most expedient way of accomplishing this would seem to be the numerical evaluation of Whipple's solution. Some steps in this direction were taken by Whipple himself, however, his work does not cover an adequate range of parameters. Furthermore, his calculations are based on a formula which results from taking the ratio of the grain-boundary diffusion coefficient to the volume diffusion constant to be infinite in certain of the places where it occurs in the exact solution. This approximation is probably quite adequate, however, it would be worthwhile to evaluate the exact solution using the value  $10^5$  for this ratio. This would confirm or deny our present speculation that taking  $\Delta = \infty$ , as Whipple has done, does not introduce a serious error. If  $\Delta = \infty$  in a satisfactory approximation the computational effort will be substantially reduced.
- (2) Validity of the Steepest Decents Approximation. As is often the case with steepest decents evaluations of integrals it is difficult to establish the range of validity of Whipple's approximate formula. One possibility is, of course, the direct comparison of the approximation with the exact numerical results discussed above. If a theorem of the form "If the approximation is valid for a concentration  $c$  then it is valid for any concentration less than  $c$ " could be established analytically, then the use of numerical comparisons to determine the range of validity would be particularly useful. A more ambitious goal and, of course, one which is less likely to be realized is the rigorous analytical determination of the range of validity of the approximation.
- (3) Analytical Approximations. A good analytical approximation to Whipple's solution with carefully established limits of validity would be extremely valuable. The hope of finding such an approximation is rather remote, however, the search should continue as a part of any sound theoretical program.



- (4) Validity of Fisher's Approximation. The range of parameters for which Fisher's approximation is valid should be established. This investigation should consider the following: the actual deduction of Fisher's formula using Whipple's solution to study the approximations which are used; the shape of the isoconcentration contours compared with the exact contours; and the validity of the activity equation used to interpret tracer study results.
- (5) Borisov's Deduction of Fisher's Formula. Borisov<sup>(3)</sup> claims to have deduced Fisher's formula from the exact solution. His presentation is sufficiently sketchy that it requires a careful reexamination. This procedure might resolve some of the questions raised above and at any rate should end the controversy which has been going on for several years.

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